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71 Applicant: E.I. DU PONT DE NEMOURS AND COMPANY
Legal Department 1007 Market Street
Wilmington, Delaware 19898(US)

72 Inventor: Goff, David Lee
419 Alliston Road
Springfield Pennsylvania 19064(US)

72 Inventor: Yuan, Edward Lung
2200 Ben Franklin Parkway Apt. 1405-N
Philadelphia Pennsylvania 19130(US)

72 Inventor: Proskow, Stephen
122 Broadbent Road Northminster
Wilmington Delaware 19810(US)

74 Representative: Woodcraft, David Charles
BROOKES & MARTIN High Holborn House 52/54 High
Holborn
London, WC1V 6SE(GB)

54 Radiation polymerizable composition for forming heat-resistant relief structures on electrical devices such as semiconductors and capacitors.

57 A polyamide ester resin containing photopolymerizable groups is made more rapidly photopolymerizable and therefore more suitable for forming relief structures on electrical devices (such as capacitors, integrated circuits and semiconductors) by including therein a radiation-sensitive polymerizable polyfunctional acrylate compound and an aromatic biimidazole photopolymerization initiator. On exposure through a pattern of a dried film obtained using a solution of such composition, photopolymerization takes place rapidly and efficiently following which developing can be effected and the photopolymerized material baked to leave a heat-resistant polyimide structure.

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RADIATION POLYMERIZABLE COMPOSITION FOR FORMING HEAT-
RESISTANT RELIEF STRUCTURES ON ELECTRICAL
DEVICES SUCH AS SEMICONDUCTORS AND CAPACITORS

This invention relates to an improved polymeric heat resistant photopolymerizable composition useful for forming relief structures on electrical devices such as semiconductors and capacitors.

Photopolymerizable polymeric compositions used to form relief structures on electrical devices are well known as shown in U.S. Patents 3,953,877, 3,957,512 and 4,040,831 (now U.S. Reissue Patent 30,186). These compositions have limited commercial use since the radiation exposure time required to photopolymerize these compositions is too long for a modern process.

Exposure times of 1 minute and preferably of 30 seconds or less are needed for an efficient process.

As will be appreciated from the Examples which follow, the invention provides compositions which can be photopolymerized in a relatively short time period of exposure to radiation. Compositions according to the invention comprise a polyamide ester resin containing photopolymerizable groups, a solvent for the resin; and the following additives:-

- (a) a radiation-sensitive polymerizable polyfunctional acrylate compound, and
- (b) an aromatic bisimidazole photopolymerization initiator.

The radiation polymerizable compositions of the invention can be used to form relief structures on electrical devices such as capacitors and semiconductors.

In practice, a solution of the composition is applied to a substrate such as a silicon wafer coated with a silicon dioxide layer and dried to form a film on the substrate. The film is then image-wise exposed to radiation through a pattern and photopolymerized to form a relief image structure. The unexposed and unpolymerized part of the film is dissolved off with a developer solution. The resulting relief structure is baked to remove the photopolymerized material and to form a polyimide structure which has been found to have a sharp definition and to have good mechanical, chemical and electrical properties.

To reduce radiation exposure time and increase the rate of photopolymerization, the composition of the invention conveniently comprises about 5-30% by weight, based on the weight of resin, of radiation sensitive polymerizable polyfunctional acrylate compound and about 0.5-15% by weight, based on the weight of the resin, of aromatic bisimidazole photopolymerization initiator.

The radiation sensitive polymerizable polyfunctional acrylate compound may, for example, be as follows:- trimethylol propane trimethacrylate, trimethylol propane triacrylate, trimethylol propane ethoxylate trimethacrylate, trimethylol propane ethoxylate triacrylate, trimethylol propane polyethoxylate trimethacrylate, trimethylol propane polyethoxylate triacrylate, pentaerythritol triacrylate, polyethylene glycol diacrylate, triethylene glycol diacrylate, polyethylene glycol dimethacrylate, polymethylene diacrylate, polymethylene dimethacrylate, trimethylene glycol dimethacrylate or a mixture of two or more thereof. Preferred are trimethylol propane polyethoxylate triacrylate having a weight average molecular weight of about 500-1500 (all molecular weights referred to herein are determined by gel permeation chromatography) as well as trimethylol propane ethoxylate triacrylate, pentaerythritol triacrylate, polyethylene glycol diacrylate, triethylene

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glycol diacrylate, polyethylene glycol dimethacrylate, polymethylene diacrylate, polymethylene dimethacrylate, and trimethylene glycol dimethacrylate.

It is possible to obtain improved results, i.e., shorter polymerization times compared to prior art compositions, without the use of the above polymerizable polyfunctional acrylate compounds in the composition. For most practical commercial processes, however, the presence of the polyfunctional acrylate compounds is highly preferred.

Typical aromatic biimidazole photo-polymerization initiators are disclosed in U.S. Patents 3,479,185 and 3,784,557. 2,4,5-Tri(optionally substituted) phenyl imidazolyl dimers having an ortho substituent on the 2-phenyl ring are particularly useful. Typical initiators of this type are 2-o-chlorophenyl-4,5-di(optionally substituted)phenylimidazolyl dimer, 2-(o-fluorophenyl)-4,5-di(optionally substituted)phenylimidazolyl dimer, 2-(o-methoxyphenyl)-4,5-di(optionally substituted)phenylimidazolyl dimer. Particularly preferred are bis(2-o-chlorophenyl-4,5-diphenylimidazolyl) and bis[2-o-chlorophenyl-4,5-di-(methoxyphenyl)imidazolyl] (e.g. the 4,5-di(-m-methoxyphenyl)imidazolyl compound), since they are stable and are excellent photopolymerization initiators.

Hexaaryl biimidazoles as disclosed in U.S. Patent 3,552,973 may also be used as initiators in compositions according to the invention.

To enhance the photopolymerization, other photoinitiators and photosensitizers in amounts of about 0.1-10% by weight, based on the weight of the resin, can be used in the composition. Typically useful photosensitizers and initiators include aromatic ketones such as tetramethyldiamino benzophenone, benzophenone, Michler's

ketone [4,4'-bis(dimethylamino)benzophenone],
4,4'-bis(diethylamino)benzophenone,
4-acryloxy-4'-diethylaminobenzophenone,
4-methoxy-4'-dimethylaminobenzophenone,
2-ethylanthraquinone, phenanthraquinone,
2-t-butylanthraquinone, 1,2-benzanthraquinone,
2,3-benzanthraquinone, 2,3-dichloronaphthoquinone,
benzil dimethyl ketal, and other aromatic ketones
such as disclosed in aforementioned U.S. Patent 3,552,973;
benzoin, benzoin ethers such as benzoin methyl ether,
benzoin ethyl ether, benzoin isobutyl ether, and
benzoin phenyl ether, methylbenzoin, ethylbenzoin and
other benzoin.

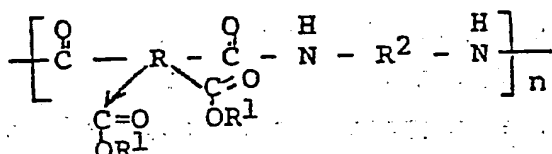
It is possible to use combinations of both
photosensitizer and photopolymerization initiators.
Generally, the photopolymerization time is longer if
the photosensitizer is not added.

It is preferred to have a compound present
that changes color when polymerization is complete
and that is a hydrogen donor that provides a rapid
start for polymerization. Leuco dyes can be used for these
purposes, such as those disclosed in aforementioned U.S. Patent
3,552,973 (col. 6, line 6 to col. 11, line 9). Typically
useful leuco dyes are alkylamino-aromatic alkanes such as
tris(diethylamino-o-tolyl) methane, tris(dimethylamino-o-
xylyl) methane, and tris(dipropylamino-o-tolyl) methane.

The photopolymerizable resin used in the
composition can be any type of resin that contains
olefinic unsaturated groups that are photopolymerizable
and that will form a polymer with good thermal, electrical
and chemical properties. Polyamide ester resins are
particularly useful. These resins are prepared according
to the aforementioned U.S. Reissue Patent 30,186 wherein
an aromatic polycarboxylic acid anhydride is esterified
with a hydroxyalkyl acrylate or methacrylate which is then
reacted with diamine. Typical aromatic polycarboxylic acid
anhydrides and diamines are disclosed in U.S. Patent 3,179,614.

Typical hydroxyalkyl acrylates and methacrylates are as follows:- hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate and hydroxybutyl methacrylate.

Typically useful polyamide ester resins have the following structure:-



where the \rightarrow denotes isomerism, R is an aromatic radical, R^1 is an organic radical containing a photo polymerizable olefinic double bond, R^2 is an aromatic, aliphatic or cycloaliphatic radical and n is a positive integer sufficiently large to provide the resin with a weight average molecular weight of about 5,000 to 75,000.

One particularly useful polyamide ester resin is the reaction product of pyromellitic dianhydride, hydroxyethyl methacrylate and oxydianiline, having in particular a weight average molecular weight of about 15,000-60,000.

Typical solvents that can be used alone or in combination to dissolve the polymer and to dilute the composition to an application viscosity are N-methylpyrrolidone, butyrolactone, ethylene glycol monoethyl ether, dimethyl formamide, dimethyl acetamide and hexamethylphosphoric acid triamide.

Preferably, the composition contains about 10-40 percent by weight, based on the weight of the composition, of polyamide ester resin containing photopolymerizable groups and about 60-90 percent by weight, based on the weight of the composition, of a solvent for the resin.

Blends of these solvents with a nonsolvent can be used as a developer solution to remove resin that was not exposed to radiation and not polymerized.

Typical developer solutions are 4-butyrolactone/toluene in a weight ratio from 2/1 to 1/4, dimethyl formamide/ethanol in a weight ratio from 2/1 to 1/4.

Plasticizers can also be added to the composition in amounts of 0.1-10% by weight, based on the weight of the resin. Typical plasticizers are tricresyl phosphate, dioctyl phthalate, dihexyl phthalate, dinonyl phthalate, polyethylene glycol ethers and ethylene glycol dicaprolate.

In applying the composition to substrates, the composition is applied and then dried to form a film at about 30 to 100°C for about 20 minutes to 5 hours. The film is then exposed through a pattern for about 1 second to 5 minutes. Preferably, for a commercial process exposure times of 1-60 seconds are required and usually an exposure time under 30 seconds is much preferred. Typical radiation sources used are ultraviolet lamps providing a wave length of 250 to 400 nanometers and an intensity of 0.5-60 milliwatts per square centimeter (mW/cm^2). After exposure, the film is then dipped or sprayed, with a developer solution, washed with a nonsolvent and then dried. The film is cured to a polyimide relief structure by baking at about 200-400°C for about 20 minutes to 4 hours. During curing all the acrylate components are decomposed leaving a polyimide structure.

The resulting relief structure has a sharp definition and good chemical, electrical and mechanical properties.

Typical uses for the composition are as follows:- protective coatings for semi-conductors, dielectric layers for multilayer integrated circuits, high temperature solder mask, bonding multilayer circuits and as a final passivating coating on electrical devices.

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The following Examples illustrate the invention. All parts and percentages are on a weight basis and molecular weights are determined by gel permeation chromatography.

EXAMPLE 1

(i) <u>Composition A</u>	<u>Grams</u>
Polyamide ester resin (polymer of pyromellitic dianhydride and esterified with hydroxy ethyl methacrylate and reacted with 4,4'-oxydianiline and having a weight average molecular weight of about 25,000 prepared according to Example 2 of above U.S. Reissue Patent 30,186)	10.00
Bis(2-o-chlorophenyl-4,5-diphenylimidazolyl)	0.70
Michler's ketone (tetramethyl diaminobenzophenone)	0.25
Tris(diethylamino-o-tolyl)methane	0.25
Trimethylol propane polyethoxylate triacrylate having a weight average molecular weight of about 1200	2.0
N-methylpyrrolidone	<u>30.00</u>
Total	43.20

The above constituents are charged into a container. The container is placed on a roller and mixed for about 2 hours and then the resulting composition is filtered through a 1 micron filter.

A 2 inch (approximately 50mm) diameter silicon wafer having a silicon dioxide coating is coated with an aminosilane adhesion promoter solution by a spin coating technique wherein the wafer is rotated at 3000 rpm for 30 seconds after the adhesion promoter solution is applied. The wafer is then placed at 300°C for 10 minutes. The above prepared Composition A is thinned as follows:- 10 parts Composition A to 1 part thinner (ethylene glycol monoethyl ether/N-methyl pyrrolidone - 1/1 weight ratio)

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and the thinned composition is applied by the above spin coating technique using 3000 rpm for 10 seconds. The composition is exposed to infrared (IR) light during the spin application. The coating of Composition A is then dried for 2 hours at 55°C to provide a film about 12,500 Angstroms thick. The coated wafer is placed in a contact printer having a 200 Watt ultraviolet (UV) light source of 356 nanometers (nm) and an intensity of about 5-6 mW/cm² using a mask with lines spaced 4 microns apart and exposed for 5 seconds. The wafer is then developed by dipping the wafer for 10 seconds in a 1/1 solution of 4-butyrolactone/toluene and then rinsed for 5 seconds with a spray of toluene to remove any unexposed composition. The wafer then is cured at 300°C for 1 hour to provide a relief structure about 4,500 Angstroms thick.

Additional silicon wafers are prepared using the above procedure except the following exposure times are used:- 10 seconds, 15 seconds, 20 seconds, 30 seconds, 45 seconds and 60 seconds. Exposure times of 10, 15 and 20 seconds result in clearly defined images which are acceptable but longer exposure times of 30, 45 and 60 seconds result in poorer images due to over exposure.

Additional silicon wafers are prepared using the above identical procedure except the following developer compositions are used:-

4-butyrolactone/toluene in the following weight ratio 1/1.2, 1/1.4 and 1/1.6. All developers were adequate and gave an acceptable product.

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(ii) Composition B which is representative of known compositions is prepared as follows:

	<u>Grams</u>
Polyamide ester resin (described above)	128.6
N-phenyl maleimide	.6.4
Michler's ketone	2.60
N-methyl pyrrolidone	<u>300.00</u>
Total	437.6

The constituents are mixed together using the same procedure as described above for Composition A and a silicon wafer is coated with the above adhesion promoter and with Composition B, both using the spin coating and drying procedures described above for Composition A. The coated wafer then is exposed as above (10,15,20,30,45 and 60 seconds) to the UV light source as used in Part (i) and developed using 1/1 ratio 4-butyrolactone/toluene developer solution. The coating is then cured as described in (i). An underexposed unacceptable relief structure is formed. Exposure time to the light source had to be increased to 3.5 minutes before an acceptable image was formed.

EXAMPLE 2

	<u>Grams</u>
Polyamide ester resin (described in Example 1)	3.000
Bis[2-o-chlorophenyl-4,5-di(methoxyphenyl)imidazolyl]	0.200
Michler's ketone	0.070
Tris(diethylamino-o-tolyl)methane	0.054
N-methyl pyrrolidone	<u>12.000</u>
Total	15.324

The above constituents are mixed together using the same procedure as in Example 1 and the resulting composition is coated onto a silicon wafer primed with an adhesion promoter as described in Example 1 using the same coating and drying procedure as in Example 1. The coated wafer then is exposed for 4.0 minutes to an ultraviolet light source of intensity 1.1 mW/cm^2 , developed, rinsed and cured as in Example 1 to provide a coating with an excellent clear image.

Composition B of Example 1 is applied as above and exposed to the same light source for the same time, developed and cured as above. An underexposed unacceptable image is formed. Exposure times had to be increased to about 5-7 minutes to form an acceptable image.

EXAMPLE 3

The following compositions are prepared by mixing the constituents as in Example 1:

<u>Composition</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
	(grams)			
Polyamide ester resin (described in Example 1)	10.0	10.0	10.0	10.0
Bis(2-o-chlorophenyl-4,5- diphenyl imidazolyl)	0.7	0.7	-	-
Michler's ketone	0.25	0.25	0.2	0.2
Benzophenone	-	-	0.8	0.8
Tris(diethylamino-o- tolyl)methane	0.20	0.20	-	-
Trimethylol propane trimethacrylate	2.0	-	2.0	-
Trimethylol propane triacrylate	-	2.0	-	2.0
N-methyl pyrrolidone	30	30	30	30
Thinner (ethylene glycol monoethyl ether/N-methyl pyrrolidone 1/1 ratio)	10	10	10	10

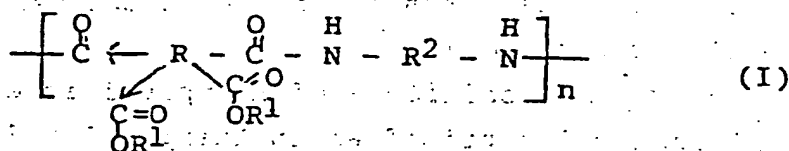
The resulting compositions are each coated onto a silicon wafer primed as in Example 1 with an adhesion promoter using the coating and baking procedure of Example 1. Each of the coatings are then exposed for 1 minute using a 200 Watt light source having a surface intensity of 1.1mW/cm^2 in the contact printer. Each of the coated wafers is developed in a 1/3 ratio 4-butyrolactone/toluene developer solution for 20 seconds, rinsed for 10 seconds with toluene and cured as in Example 1. All wafers have acceptable images. The wafer made with Composition D has the best and most clear image. The wafer made with Composition C has the next best image. The image on the wafer made with Composition F is slightly better than the image on the wafer made with Composition E.

Composition B of Example 1 is coated onto a silicon wafer primed as in Example 1 using the above procedure. A 1 minute exposure time gave an underexposed unacceptable image. Exposure times had to be increased to about 5-7 minutes to provide a clear and distinct image on the wafer.

1. A radiation polymerizable composition comprising a polyamide ester resin containing photopolymerizable groups, a solvent for the resin, a radiation-sensitive polymerizable polyfunctional acrylate compound and an aromatic bisimidazole photopolymerization initiator.

2. A composition as claimed in Claim 1 wherein the polymerizable polyfunctional acrylate compound is present in an amount of 5-30% by weight, based on the weight of the resin, and the photopolymerization initiator is present in an amount of 0.5-15% by weight, based on the weight of the resin.

3. A composition as claimed in Claim 1 or Claim 2 wherein the polyamide ester resin has the following structure:-



wherein \longrightarrow denotes isomerism, R is an aromatic radical, R^1 is an organic radical containing a photopolymerizable olefinic bond, R^2 is an aromatic, aliphatic or cycloaliphatic radical and n is an integer sufficiently large to provide the resin with a weight average molecular weight of about 5,000 to 75,000 determined by gel permeation chromatography.

4. A composition as claimed in Claim 3 wherein the polyamide ester resin has the structural formula (I) in which R is the residue $\text{> (C}_6\text{H}_2\text{) <}$ of pyromellitic dianhydride, R¹ is the residue of hydroxyalkyl methacrylate or hydroxyalkyl acrylate and -NH-R²-NH- is the residue of an aromatic diamine.

5. A composition as claimed in any preceding claim wherein the polymerizable polyfunctional acrylate is trimethylol propane trimethacrylate, trimethylol propane triacrylate, trimethylol propane ethoxylate trimethacrylate, trimethylol propane ethoxylate

triacrylate, trimethylol propane polyethoxylate trimethacrylate, trimethylol propane polyethoxylate triacrylate, pentaerythritol triacrylate, polyethylene glycol diacrylate, triethylene glycol diacrylate, polyethylene glycol dimethacrylate, polymethylene diacrylate, polymethylene dimethacrylate, trimethylene glycol dimethacrylate or a mixture of two or more thereof.

6. A composition as claimed in any preceding claim wherein the photopolymerization initiator is bis(2-o-chlorophenyl-4,5-diphenylimidazolyl) or bis[2-o-chloro-phenyl-4,5-di(methoxyphenyl)imidazolyl].

7. A composition as claimed in any preceding claim and including 0.1-10% by weight, based on the weight of the resin, of a leuco dye.

8. A composition as claimed in Claim 7 in which the leuco dye is an alkyl amino-aromatic alkane.

9. A composition as claimed in any preceding claim and including 0.1-10% by weight, based on the weight of the resin, of a photosensitizer (in addition to the initiator).

10. A composition as claimed in any preceding claim wherein the polyamide ester resin is the product of esterifying pyromellitic dianhydride with hydroxyethyl methacrylate and reacting the resulting ester with oxydianiline; the polyfunctional acrylate compound is trimethylol propane polyethoxylate having a weight average molecular weight of about 500-1500; the photopolymerization initiator is bis(2-o-chlorophenyl-4,5-diphenylimidazolyl); and the composition contains about 0.1-10% by weight, based on the weight of the resin, of tris(diethylamino-o-tolyl) methane, and about 0.1-10% by weight, based on the weight of the resin, of tetramethyldiamino benzophenone photosensitizer.

11. A composition as claimed in any one of claims 1 to 9 wherein the polyamide ester is the product of esterifying pyromellitic dianhydride with hydroxyethyl methacrylate and reacting the resulting ester with

oxydianiline; the polyfunctional acrylate is trimethylol propane trimethacrylate or trimethylol propane triacrylate; the polymerization initiator is bis(2-o-chlorophenyl-4,5-diphenylimidazolyl); and the composition contains about 0.1-10% by weight, based on the weight of the resin, of tris(diethyl amino-o-tolyl) methane and about 0.1-10% by weight, based on the weight of the resin, of tetramethyldiamino benzophenone photosensitizer.

12. An electrical device coated with a polymerized polyimide structure layer resulting from the composition of any preceding claim.

13. The electrical device of Claim 12 which is a capacitor, semiconductor, multilayer circuit or an integrated circuit.

14. A radiation polymerizable composition comprising a polyamide ester resin containing photopolymerizable groups, a solvent for the resin and an aromatic bisimidazole photopolymerization initiator.

15. A composition as claimed in Claim 14 wherein the resin has the structural formula defined in Claim 3 or Claim 4.

16. A composition as claimed in Claim 15 wherein the polyamide ester resin is the product of esterifying pyromellitic dianhydride with hydroxyethyl methacrylate and reacting the resulting ester with oxydianiline; the photopolymerization initiator is bis[2-o-chlorophenyl-4,5-di(methoxyphenyl)imidazolyl]; and the composition contains about 0.1-10% by weight of a tetramethyldiamino benzophenone photosensitizer.

17. A radiation-polymerizable composition comprising a polyamide ester resin containing photopolymerizable groups, a solvent for the resin, a photoinitiator and a polymerizable polyfunctional acrylate compound.

18. A composition as claimed in Claim 17 wherein the polyfunctional acrylate compound is present

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in an amount of from 5% to 30% by weight based on the weight of the resin.

19. A method for the formation of a relief structure on an electrical device which method comprises applying to the substrate of the device a solution of a radiation-sensitive polyamide ester resin composition containing (i) said resin, (ii) a radiation-sensitive polymerizable polyfunctional acrylate compound, and (iii) an aromatic bisimidazole photopolymerization initiator; drying the composition; exposing the composition to radiation through a pattern; dissolving unirradiated portions; and baking the resulting relief structure to form a heat-resistant polyimide structure..

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